Electrochemical Electron Spin Resonance using a Tube Electrode

By W. John Albery,* Barry A. Coles, Aitken M. Couper, and Kevin M. Garnett

(Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ)

Summary Radical species generated on a tube electrode are transported under known conditions of laminar flow from the electrode into the e.s.r. cavity immediately below the electrode; the use of laminar flow allows the solution of the convective diffusion equation describing the transport and hence the e.s.r. signal can be interpreted in terms of the flux of material at the electrode.

The use of e.s.r. to investigate electrochemical intermediates[1] is more quantitative if the signal strength can be interpreted in terms of the flux of the intermediate leaving the electrode surface. We have constructed an apparatus in which this is possible. The solution flows under gravity down a cylindrical Spectrosil tube of 1 mm diameter. An annular gold electrode which is flush with the side of the tube is placed immediately above the e.s.r. cavity. The flow in the tube both past the electrode and through the cavity is laminar, with the usual parabolic distribution. The convective diffusion equation which describes the transport of species from the electrode and their distribution in the cavity can be solved analytically. We take the particular case when the bottom edge of the electrode coincides with the top edge of the cavity. Integrating across the tube we can calculate the number of spins at any distance below the electrode. The cavity sensitivity is assumed to vary as a $\cos^2$ function about the centre of the cavity. Convolution of the number of spins with the $\cos^2$ function gives equation (1) where L is the "peak to peak"

$$L = 0.53 \, S_0 \, l^{\frac{5}{3}} \, ir^2/(nFD^{\frac{1}{3}}V^{\frac{2}{3}}) \tag{1}$$

amplitude of the e.s.r. signal, S_0 is the "peak to peak" signal amplitude of a point source of 1 mol of spins at the

centre of the cavity, V is the flow rate in cm^3 s^{-1}, l is the length of the cavity, i is the generating current on the electrode, r is the radius of the tube, D is the diffusion coefficient of the radical, and n is the number of electrons involved in the generation of the radical. Both the electrochemistry and the e.s.r. are studied in a steady state.
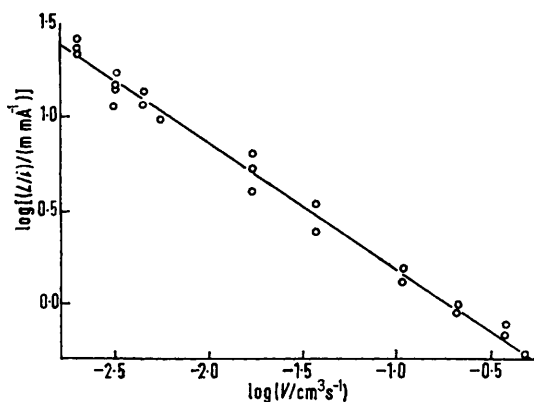

FIGURE 1. Plot of equation (1) as $\log[(L/i)/(m\ mA^{-1})]$ against $\log(V/cm^3\ s^{-1})$. The gradient is $-2/3$.

Figure 1 shows results for the reduction of nitrobenzene on a gold electrode in an aqueous solution which was 1M in NaOH. 54 Lines of the e.s.r. spectrum of $PhNO_2^-$ are fully resolved at all flow rates. The results are plotted according to equation (1) as $\log(L/i)$ against $\log V$. The gradient is $-2/3$ and equation (1) is obeyed over two orders of magnitude. The intercept from Figure 1 differs by about $\log(2)$ from the value calculated from equation (1). This discrepancy is probably caused by uncertainty in our estimation of S_0 using standardized coal samples which had to be carried out with the electrode not present.

Figure 2 shows the variation of L (at constant V) with the generating current on the electrode. The results agree with those obtained using a gold ring-disc electrode which are
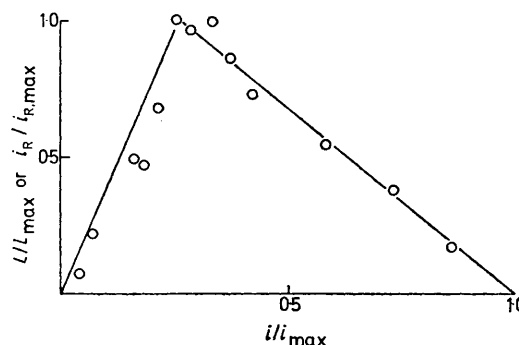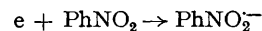

FIGURE 2. Plot of (L/L_{max}), $\bigcirc$, or $(i_R/i_{R,max})$, (solid line), against (i/i_{max}) where i_R is the ring current, i is the current on the tube or on the disc electrode, and i_{max} is the limiting current on either electrode.

shown by the line. The maximum occurs at $\frac{1}{4}$ of the limiting current since the two possible electrode[2] reactions are:

$$e + PhNO_2 \rightarrow PhNO_2^-$$

and $3e + 4H^+ + PhNO_2^- \rightarrow PhNHOH + H_2O.$

For the first quarter the main product is the radical anion; thereafter more and more PhNHOH is formed and less and less radical until at the limiting current PhNHOH is the only product and no radical anion escapes to be detected on either the ring electrode or by e.s.r. The tube-e.s.r. technique is, at the moment, somewhat less precise than the ring-disc electrode, but one can obtain more information about the nature of the radical intermediates from the fine structure of an e.s.r. spectrum than from a half-wave potential. A combination of the two techniques should be particularly powerful.

[1] B. Kastening, B. Gostisa-Mihelcic, and J. Divisek, Faraday Discuss., in the press.
[2] L. N. Nekrasov and B. G. Podlibner, Soviet Electrochem., 1970, 6, 207.